Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 16.* Synthesis, Structure,† and Solid-state Phosphorus-31 Nuclear Magnetic Resonance Spectra of some Novel [Cu₄X₄L₄] (X = Halogen, L = N, P Base) 'Cubane' Clusters

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Recrystallization of $[Cu_4I_4(PPh_3)_4]$ from toluene has yielded a new polymorph of that compound, (1), which has been shown by single-crystal X-ray diffraction analysis to have a tetrametallic 'cubane' structure rather than the expected 'step' structure. Crystals are monoclinic, space group $P2_1/n$, with $a = 19.47(1)$, $b = 26.94(1)$, $c = 13.528(5)$ Å, $\beta = 98.98(4)°$, $Z = 4$ tetramers; R was 0.06 for $N_o = 3\,681$. Cu–I distances range from 2.653(3) to 2.732(3) Å, with Cu$\cdots$Cu 2.874(5)—3.164(4) and I$\cdots$I 4.234(2)—4.496(3) Å. All adducts of stoicheiometry $[M_4X_4(PPh_3)_4]$ (M = Cu or Ag; X = Cl, Br, or I) have now been synthesized and structurally characterized in a cubane configuration. Recrystallization of copper(I) chloride and bromide from triethylamine also yields tetrameric cubane 1 : 1 adducts [X = Cl (2) or Br (3)], as does the reaction of copper(I) chloride with the very bulky ligand 2-[bis(trimethylsilyl)methyl]pyridine, to give $[Cu_4Cl_4(tmspy)_4]$ (4). These three complexes have also been crystallographically characterized, (2) and (4) being the first reported cubane type tetramers for the copper(I) chloride–nitrogen base system. Complexes (2) and (3) are isostructural with their triethylarsine and -phosphine counterparts, being cubic, space group $I\bar{4}3m$, with $a = 12.162(5)$ Å in (2) and 12.368(3) Å in (3); $Z = 2$ tetramers. Cu–Cl,Br distances are 2.441(4) and 2.537(3) Å respectively. For (4), the crystals are tetragonal, space group $I4_1/a$, with $a = 18.620(4)$, $c = 20.079(5)$ Å, $Z = 4$ tetramers. Although the Cu_4Cl_4 cubane core of the molecule has crystallographically imposed $\bar{4}$ symmetry, the geometry is very unsymmetrical as a consequence of the ligand bulk, with Cu–Cl 2.225(2)—2.636(2), Cu$\cdots$Cu 2.960(2)—3.194(2), and Cl$\cdots$Cl 3.838(3)—3.866(3) Å. Residuals R for (2), (3), (4) were 0.040, 0.038, and 0.040 respectively for $N_o = 136, 136$, and 1 008 'observed' reflections. The solid-state ^{31}P n.m.r. spectra of the triphenylphosphine cubane clusters show significant differences to those with a 'step' geometry; these differences are related to the crystallographic environment of the phosphorus nuclei.

Over the last decade, the systems of 1 : 1 adducts of copper(I) and silver(I) halides with monodentate tertiary phosphine and arsine bases (L) have been widely studied with all possible halides (X) and a variety of sterically active bases. These adducts crystallize as discrete tetrametallic clusters which exhibit an isomerism between the closed pseudo-'cubane' form, initially described by Wells for [{CuI(AsEt₃)}₄],[1] and the open 'step' form.

Theoretical calculations on [Ag₄X₄(PPh₃)₄] (X = Cl,[2] Br,[3] or I[4]) showed that for copper(I) and silver(I) halides with triphenylphosphine, the occurrence of the cubane cluster with [Ag₄X₄(PPh₃)₄] and with [Cu₄Cl₄(PPh₃)₄],[5] and the observation of the step cluster for [Cu₄Br₄(PPh₃)₄]·2CHCl₃[6] and [Cu₄I₄(PPh₃)₄],[7] could be rationalized in terms of the appropriate steric parameters of the metal, halide, and base. Recently, however, following the observation of solid-state ^{31}P n.m.r. spectra for [Cu₄Br₄(PPh₃)₄] which did not conform to the expectations of the step cluster, we showed that the polymorph of that compound recrystallized from toluene was, in fact, the cubane isomer.[8] We have since achieved a new crystalline polymorph of the iodide analogue, [Cu₄I₄(PPh₃)₄]

'cubane' cluster　　　'step' cluster

'stair' polymer　　　'linked cube' polymer
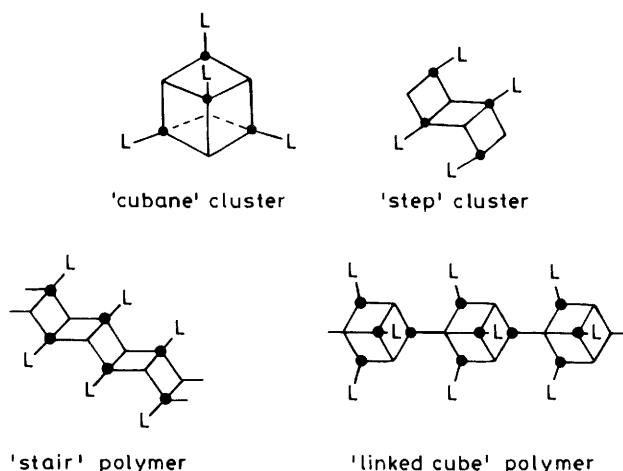
(1), by recrystallization from toluene and have shown that it also is of the cubane structural type.

In contrast to this work, it is only recently that the structures of 1 : 1 adducts of copper(I) halides with monodentate nitrogen bases have been described, despite considerable earlier literature on their synthesis. For copper(I) iodide adducts, a number of cubane type clusters have been reported.[9–13] The 'step' isomer is, however, unknown (except for the stoicheiometry

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Table 1. Non-hydrogen atom parameters for (1)*

Atom	x	y	z
I(1)	0.314 92(8)	0.063 04(5)	0.322 66(11)
I(2)	0.133 79(8)	0.138 33(6)	0.429 26(11)
I(3)	0.221 91(9)	0.191 20(6)	0.172 13(12)
I(4)	0.345 50(8)	0.199 06(6)	0.480 20(11)
Cu(1)	0.221 5(1)	0.206 3(1)	0.365 8(2)
Cu(2)	0.269 3(2)	0.114 7(1)	0.471 2(2)
Cu(3)	0.193 4(2)	0.109 7(1)	0.274 4(2)
Cu(4)	0.338 1(2)	0.160 8(1)	0.295 0(2)
Ligand 1			
P	0.179 2(3)	0.281 9(2)	0.396 1(4)
C(A1)	0.196 7(10)	0.297 7(8)	0.528 8(15)
C(A2)	0.191 2(12)	0.260 3(9)	0.595 6(18)
C(A3)	0.208 1(13)	0.268 5(10)	0.700 1(19)
C(A4)	0.223 8(14)	0.314 8(12)	0.733 5(21)
C(A5)	0.228 9(16)	0.353 4(12)	0.664 4(27)
C(A6)	0.215 6(15)	0.341 6(12)	0.561 4(24)
C(B1)	0.211 1(12)	0.336 0(8)	0.335 5(16)
C(B2)	0.174 9(12)	0.378 4(9)	0.317 4(16)
C(B3)	0.202 7(13)	0.418 5(9)	0.274 6(18)
C(B4)	0.269 1(13)	0.415 5(9)	0.247 6(17)
C(B5)	0.303 0(13)	0.372 1(11)	0.261 6(19)
C(B6)	0.274 3(13)	0.330 9(9)	0.306 3(18)
C(C1)	0.087 6(11)	0.286 6(8)	0.357 5(17)
C(C2)	0.041 4(15)	0.287 4(10)	0.419 8(19)
C(C3)	−0.030 2(16)	0.286 8(11)	0.388 4(23)
C(C4)	−0.055 2(13)	0.284 5(10)	0.288 6(22)
C(C5)	−0.010 8(16)	0.285 0(10)	0.221 7(20)
C(C6)	0.060 4(15)	0.282 6(10)	0.259 3(21)
Ligand 2			
P	0.287 9(3)	0.070 6(2)	0.614 3(4)
C(A1)	0.375 2(12)	0.052 1(9)	0.657 5(16)
C(A2)	0.393 6(13)	0.011 6(9)	0.724 1(17)
C(A3)	0.463 2(15)	−0.000 9(10)	0.751 8(19)
C(A4)	0.512 0(16)	0.022 5(12)	0.717 6(23)
C(A5)	0.499 1(18)	0.062 1(13)	0.658 4(25)
C(A6)	0.427 3(16)	0.076 0(10)	0.626 0(20)
C(B1)	0.242 2(10)	0.010 2(8)	0.613 3(16)
C(B2)	0.198 1(13)	−0.004 4(9)	0.679 4(19)
C(B3)	0.166 2(13)	−0.050 2(10)	0.669 2(19)
C(B4)	0.179 5(13)	−0.082 5(9)	0.598 5(19)
C(B5)	0.219 9(12)	−0.068 8(9)	0.531 3(18)
C(B6)	0.253 1(12)	−0.022 1(9)	0.536 4(17)
C(C1)	0.260 6(11)	0.104 0(8)	0.718 4(15)
C(C2)	0.310 2(11)	0.118 3(8)	0.801 7(17)

Atom	x	y	z
C(C3)	0.283 9(13)	0.146 4(9)	0.877 3(17)
C(C4)	0.219 6(14)	0.156 6(9)	0.875 1(18)
C(C5)	0.168 7(12)	0.142 2(8)	0.793 4(17)
C(C6)	0.192 0(11)	0.116 2(8)	0.717 8(15)
Ligand 3			
P	0.114 6(3)	0.065 0(2)	0.171 5(3)
C(A1)	0.152 2(11)	0.027 5(8)	0.081 3(15)
C(A2)	0.133 7(11)	−0.021 7(8)	0.056 2(16)
C(A3)	0.163 3(11)	−0.047 6(9)	−0.009 1(17)
C(A4)	0.214 3(12)	−0.026 7(9)	−0.053 2(17)
C(A5)	0.235 8(13)	0.021 9(10)	−0.032 1(18)
C(A6)	0.204 3(12)	0.046 3(8)	0.036 1(18)
C(B1)	0.063 0(10)	0.022 4(7)	0.233 7(15)
C(B2)	0.090 1(11)	0.004 0(8)	0.331 3(16)
C(B3)	0.050 6(15)	−0.027 3(10)	0.380 5(20)
C(B4)	−0.013 8(14)	−0.043 4(9)	0.332 4(20)
C(B5)	−0.038 7(13)	−0.029 3(9)	0.238 1(19)
C(B6)	−0.001 7(12)	0.003 9(9)	0.188 9(17)
C(C1)	0.046 4(12)	0.103 4(8)	0.095 3(18)
C(C2)	0.040 7(13)	0.103 5(9)	−0.009 9(19)
C(C3)	−0.010 0(15)	0.138 3(11)	−0.060 4(20)
C(C4)	−0.048 0(15)	0.164 9(11)	−0.007 3(24)
C(C5)	−0.044 7(17)	0.163 5(12)	0.090 5(27)
C(C6)	0.005 2(18)	0.134 5(13)	0.145 3(24)
Ligand 4			
P	0.441 0(4)	0.175 6(2)	0.243 6(5)
C(A1)	0.449 8(13)	0.235 5(8)	0.184 9(16)
C(A2)	0.513 1(14)	0.256 4(10)	0.174 5(19)
C(A3)	0.515 5(15)	0.301 2(12)	0.121 8(21)
C(A4)	0.460 0(19)	0.324 0(11)	0.081 9(22)
C(A5)	0.396 0(18)	0.304 2(13)	0.086 4(24)
C(A6)	0.392 1(16)	0.260 2(12)	0.141 0(23)
C(B1)	0.464 8(13)	0.130 9(9)	0.150 0(17)
C(B2)	0.414 4(12)	0.102 9(9)	0.098 4(19)
C(B3)	0.433 2(15)	0.071 3(10)	0.023 7(21)
C(B4)	0.494 2(16)	0.071 6(10)	0.004 5(20)
C(B5)	0.548 1(15)	0.098 7(11)	0.051 5(22)
C(B6)	0.533 2(15)	0.129 8(11)	0.134 6(21)
C(C1)	0.514 7(12)	0.173 2(10)	0.347 8(18)
C(C2)	0.537 6(16)	0.215 1(11)	0.402 8(22)
C(C3)	0.591 1(16)	0.211 7(12)	0.483 1(23)
C(C4)	0.617 1(16)	0.166 1(14)	0.506 9(24)
C(C5)	0.596 3(17)	0.126 1(13)	0.459 7(25)
C(C6)	0.541 8(13)	0.129 9(12)	0.375 5(24)

* Estimated standard deviations are given in parentheses here and in the other Tables.

$[Cu_4I_4L_6][L = $ 2-methylpyridine (2Me-py)[14]], and instead has its counterpart in the 'stair' polymer.[15]

With triethylamine, the nitrogen analogue of the archetypal triethylphosphine and triethylarsine ligands, copper(I) iodide yields not the expected cubane cluster, but rather the novel $[\{Cu_4I_4(NEt_3)_3\}_\infty]$ 'linked cube' polymer.[14] For copper(I) bromide and chloride adducts, the data are much sparser: the structure of the cubane complex $[Cu_4Br_4(2Me\text{-}py)_4]$ has been reported,[16] while the existence of the cubane form has been inferred for complexes of N,N-diethylnicotinamide, but these have not been described structurally.[12] The adduct of copper(I) chloride with pyridine (recrystallized from acetone) yields the stair polymer, and its copper(I) bromide analogue is isomorphous.[17] As part of our general programme of investigation into the chemistry of these systems we have reacted triethylamine with copper(I) chloride and bromide under an argon atmosphere to produce polycrystalline materials which have been characterized structurally as cubane

L—◇—L

'dimeric' cluster

L　L　L

'single strand' polymer
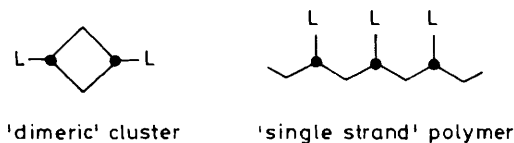
type clusters $[Cu_4X_4(NEt_3)_4]$ [X = Cl (2) or Br (3)]; the chloride (2) is the first such structurally characterized example.

By appropriate modification of the relative nature of the metal, halide, base, and solvent, the cubane or step clusters may be severed to yield 'dimeric' clusters, and the stair polymer to yield 'single strand' (or 'half stair') polymers.

In order to examine the effects of base on the type of configuration adopted we have also investigated the reaction of the extremely bulky ligand, 2-[bis(trimethylsilyl)methyl]pyridine with copper(I) chloride, $[Cu_4Cl_4(tmspy)_4]$ (4). Given the above variety of possible products, plus the potential to form

monomeric and dimeric 2:1 complexes,[18] it was of considerable interest to us that the exclusive crystalline product from the reaction mixture was the 1:1 cubane type cluster. In this paper we report details of the synthesis of these four novel cubane clusters and their structural characterization by single-crystal X-ray diffraction. We also report the solid-state [31]P n.m.r. spectrum of (1) and compare it with that of the previously reported isomeric step structure for $[Cu_4Br_4(PPh_3)_4]$.[8]

Experimental

Preparation of Complexes.—$[Cu_4I_4(PPh_3)_4]$ (1). Copper(I) iodide (1.9 g, 0.01 mol) and PPh_3 (2.62 g, 0.01 mol) were refluxed overnight in toluene (250 cm³) redistilled from CaH_2. Very slow cooling (overnight) of the resultant clear solution to room temperature resulted in well formed crystals of the complex.

$[Cu_4X_4(NEt_3)_4][X = Cl (2) or Br (3)]$. Both complexes were prepared by the dissolution of copper(I) halide (0.2 g) in warm (ca. 40 °C) excess oxygen-free triethylamine, redistilled from KOH, under an atmosphere of argon. Slow cooling of the resultant pale blue, clear solution to −30 °C produced well formed crystals of the complexes. Since the crystals readily lost base and oxidized rapidly on exposure to the atmosphere, crystals for structure analysis were transferred under an argon atmosphere to capillaries containing mother-liquor.

$[Cu_4Cl_4(tmspy)_4]$ (4). The ligand tmspy was prepared by a one-step synthesis from 2-methylpyridine using $LiBu^n$-$(Me_2NCH_2CH_2NMe_2)$, then $SiMe_3Cl$.[19] The 1:1 adduct of the ligand with copper(I) chloride was prepared by the dissolution of the halide in ca. four mol equiv. of tmspy at ca. 80 °C under an argon atmosphere, followed by the addition of an equivalent volume of hexane and cooling the solution to −30 °C overnight. The 1:1 adduct was the exclusive product. Even under more forcing conditions, there was no evidence for a 1:2

complex or other metal halide:ligand combination. The crystal used for X-ray analysis was mounted from the mother-liquor in a capillary under argon.

Crystallography.—*Crystal data for* $[Cu_4I_4(PPh_3)_4]$ (1). $C_{72}H_{60}Cu_4I_4P_4$, $M = 1\ 809.6$, monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14), $a = 19.47(1)$, $b = 26.94(1)$, $c = 13.528(5)$ Å, $\beta = 98.98(4)°$, $U = 7\ 008(5)$ Å³, $D_m = 1.74(1)$, D_c ($Z = 4$ tetramers) $= 1.72$ g cm⁻³, $F(000) = 3\ 520$, $\mu_{Mo} = 31.6$ cm⁻¹. Specimen: $0.15 \times 0.15 \times 0.20$ mm; $2\theta_{max.} = 45°$, $N = 9\ 211$, $N_o = 3\ 681$, $R = 0.060$, $R' = 0.050$. No extinction correction was made.

Crystal data for $[Cu_4Cl_4(NEt_3)_4]$ (2). $C_{24}H_{60}Cl_4Cu_4N_4$, $M = 800.7$, cubic, space group $I\bar{4}3m$ (T^3_d, no. 217), $a = 12.162(5)$ Å, $U = 1\ 799(1)$ Å³, D_c ($Z = 2$) $= 1.48$ g cm⁻³, $F(000) = 832$, $\mu_{Mo} = 27.4$ cm⁻¹. Specimen: approximated as spheroid of radius 0.11 mm for absorption correction purposes; $2\theta_{max.} = 50°$, $N = 191$, $N_o = 136$, $R = 0.040$, $R' = 0.045$.

Crystal data for $[Cu_4Br_4(NEt_3)_4]$ (3). $C_{24}H_{60}Br_4Cu_4N_4$, $M = 978.6$, $I\bar{4}3m$, $a = 12.368(3)$ Å, $U = 1\ 892.0(8)$ Å³, D_c ($Z = 2$) $= 1.72$ g cm⁻³, $F(000) = 976$, $\mu_{Mo} = 65$ cm⁻¹. Specimen: spheroid of radius 0.10 mm; $2\theta_{max.} = 50°$, $N = 198$, $N_o = 136$, $R = 0.038$, $R' = 0.040$.

Crystal data for $[Cu_4Cl_4(tmspy)_4]$ (4). $C_{48}H_{92}Cl_4Cu_4N_4Si_8$, $M = 1\ 348$, tetragonal, space group $I4_1/a$ (C^6_{4h}, no. 88), $a = 18.620(4)$, $c = 20.079(5)$ Å, $U = 6\ 962(3)$ Å³, D_c ($Z = 4$) $= 1.29$ g cm⁻³, $F(000) = 2\ 816$, $\mu_{Mo} = 14.6$ cm⁻¹ (analytical absorption correction). Specimen: $0.50 \times 0.38 \times 0.36$ mm; $2\theta_{max.} = 40°$, $N = 1\ 624$, $N_o = 1\ 008$, $R = 0.040$, $R' = 0.048$. No extinction correction was made.

Unique data sets were measured at 295 K using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with graphite-monochromated Mo-K_α radiation sources and operating in conventional $2\theta/\theta$ scan mode. Within the specified $2\theta_{max.}$ limit, N independent reflections were obtained, N_o with $I > 2\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after absorption correction. For (2) and (3), refinement was initiated successfully using the parameters of the analogue, $[Cu_4I_4(AsEt_3)_4]$ (or its inverse as appropriate), indicating an isomorphous description to be suitable, the present disorder model for the ethyl groups also being based on that compound. Residuals R, R' on $|F|$ are quoted at convergence for the preferred chirality, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral complex scattering factors were used;[20] computation used the X-RAY 76 program system[21] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Atomic co-ordinates are given in Tables 1—3. Hydrogen atoms were included at idealized positions as constrained estimates. No disorder was found, other than that of the ethyl group. For (1), the rather weak and limited data would not support anisotropic refinement of the thermal parameters of all non-hydrogen atoms; accordingly for the carbon atoms, the appropriate isotropic form was used. For (2) and (3), the effects of extinction were significant and the Larson

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Table 2. Non-hydrogen atom parameters for (2) and (3); values for (3) are given in square brackets below the corresponding value for (2); the crystal for (3) is of opposite chirality to that of (2); the population of C(1) is 0.5

Atom	Site symmetry	x	y	z
Cu	$3m$	0.589 1(1)	*	*
		[0.413 1(2)]	*	*
Cl	$3m$	0.390 6(1)	*	*
Br	$3m$	[0.614 5(1)]	*	*
N	$3m$	0.686 7(8)	*	*
		[0.316 9(11)]	*	*
C(1)	1	0.790(2)	0.636(2)	0.713(2)
		[0.216(2)]	[0.366(2)]	[0.289(3)]
C(2)	m	0.608(1)	*	0.864(1)
		[0.394(1)]	*	[0.141(2)]

* Symmetry-related terms.

Table 3. Non-hydrogen atom co-ordinates for (4)

Atom	x	y	z	Atom	x	y	z
Cu	0.034 43(5)	0.321 65(5)	0.685 07(6)	Si(1)	0.000 8(1)	0.459 4(1)	0.859 3(1)
Cl	0.060 59(10)	0.334 31(9)	0.557 91(10)	C(8)	−0.090 0(4)	0.499 7(4)	0.872 1(4)
N(1)	0.112 6(3)	0.379 5(3)	0.725 7(3)	C(9)	0.065 2(5)	0.505 1(6)	0.917 6(4)
C(2)	0.179 2(4)	0.355 5(4)	0.715 4(4)	C(10)	−0.003 8(5)	0.362 4(5)	0.878 2(5)
C(3)	0.240 8(4)	0.391 5(5)	0.735 1(4)	Si(2)	0.007 6(1)	0.551 9(1)	0.722 3(1)
C(4)	0.231 5(4)	0.453 2(5)	0.767 3(4)	C(11)	0.056 0(5)	0.549 0(5)	0.641 5(4)
C(5)	0.164 1(4)	0.479 3(4)	0.778 6(4)	C(12)	−0.089 9(5)	0.552 3(4)	0.703 7(4)
C(6)	0.103 1(4)	0.442 0(3)	0.757 6(3)	C(13)	0.031 7(5)	0.635 6(4)	0.769 7(5)
C(7)	0.027 4(3)	0.467 7(3)	0.770 1(3)				

extinction parameter was refined to 3.9(4) × 10^{-4}, 7.0(4) × 10^{-4}. The structures of (1) and (4) are shown in Figures 1 and 2 respectively.

Solid-state [31]P *N.M.R. Spectroscopy.*—Spectra were obtained on a Brüker CXP-300 spectrometer at 121.47 MHz using [1]H-^{31}P cross-polarization with radio frequency fields of 8 and 20 G for ^{1}H and ^{31}P respectively. Single contacts of 1 ms were used with spin temperature alternation and recycle times of between 10 and 50 s, depending on the ^{1}H spin-lattice relaxation times. Samples were packed in Delrin rotors and spun at speeds of between 3.0 and 4.0 kHz at the magic angle. A sweep width of 20 kHz with a total acquisition time of 12.8 ms was used. Between 20 and 200 free induction decays were collected, zero filled to 8 K and transformed with an experimental line broadening of 10—50 Hz. Chemical shift data are referenced to 85% H_3PO_4.

Results and Discussion

Single-crystal X-ray determination on (1) establishes the asymmetric unit of the cell to consist of a single tetramer, consistent with the stoicheiometry and connectivity of the cubane isomer. *All* adducts of stoicheiometry $[M_4X_4(PPh_3)_4]$ (M = Cu or Ag; X = Cl, Br, or I) have now been structurally characterized and confirmed thus. The existence of this form *vis-à-vis* the step isomer, instead of being clear-cut in terms of the relative steric parameters of metal, halide, and ligand as was once suggested on theoretical grounds,[4] must now be seen as a complex compromise in which the properties of the solvent and the methods of sample preparation and recrystallization play a significant part. For example, although recrystallization of 1:1 stoicheiometric ratios of copper(i) iodide and triphenyl-phosphine from toluene and chloroform normally yields the cubane and step isomers respectively, on occasion crystals of other species such as the 2:3 dimer can also be isolated (see also ref. 7). With acetonitrile as a solvent the situation is even more complex and the crystalline products from the reaction mix-

tures invariably contain significant percentages of monomeric $[CuI(PPh_3)_2]$, dimeric $[Cu_2I_2(PPh_3)_3]$, and the solvated tetrameric step cluster. It is of interest to note that our attempts to date to isolate the as yet uncharacterized step cluster for $[Cu_4Cl_4(PPh_3)_4]$ have resulted only in the formation of the cubane cluster or the 2:3 dimer, an experience paralleled by that found for the reaction of copper(i) iodide with triphenyl-arsine.[7,22] Trends throughout the series of cubane clusters, in terms of geometric parameters are summarized in Table 4 [the
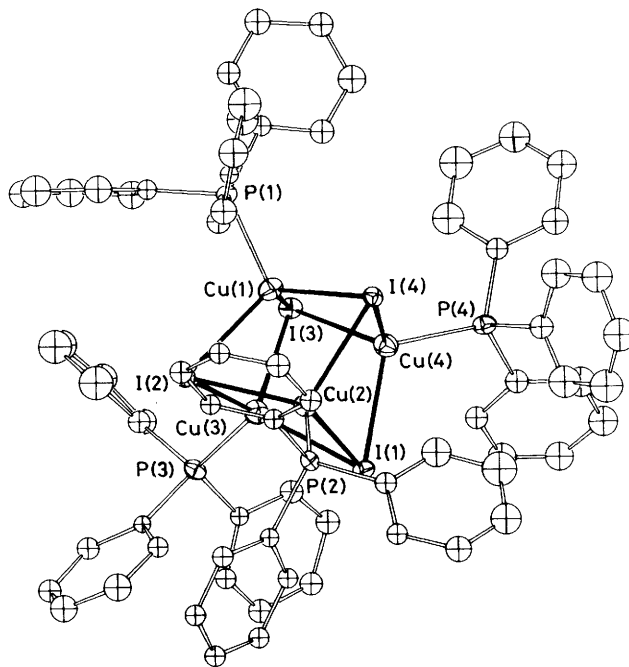

Figure 1. The tetramer of (1); 20% thermal ellipsoids are shown for Cu and I and spheroids of the other non-hydrogen atoms
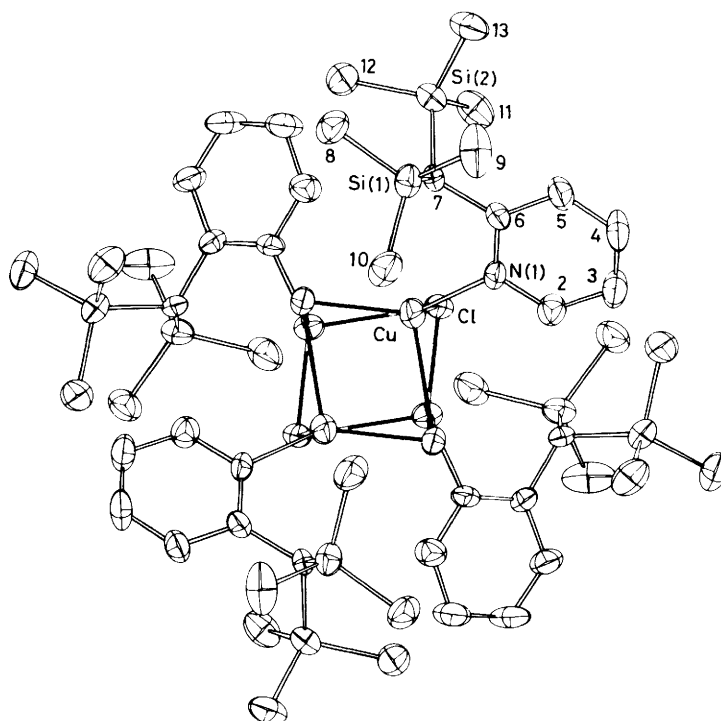

Figure 2. Projection of the tetramer of (4) down the unique crystallographic axis, showing the non-hydrogen atom labelling and 20% thermal ellipsoids

Table 4. $[M_4X_4L_4]$ pseudo-cubane core parameters; ranges are given where appropriate

Compound	Symmetry	Distances (Å)				Angles (°)		
		M–X	M–L	M···M	X···X	M–X–M	X–M–X	L–M–X
$[Cu_4Cl_4(NEt_3)_4]$[a]	$\bar{4}3m$	2.441(4)	2.054(5)	3.069(1)	3.764(2)	77.92(7)	100.90(8)	117.1(2)
$[Cu_4Cl_4(tmspy)_4]$[a]	$\bar{4}$	2.225(2)	1.986(5)	2.960(2)	3.838(3)	74.51(6)	94.07(7)	102.5(2)
		−2.636(2)		−3.194(2)	−3.866(3)	−82.28(7)	−105.09(8)	−138.8(2)
$[Cu_4Br_4(NEt_3)_4]$[a]	$\bar{4}3m$	2.537(3)	2.059(8)	3.041(2)	4.005(2)	73.64(6)	104.22(6)	114.3(3)
$[Cu_4Br_4(2Me-py)_4]$[b]	1	2.435(2)	2.05(1)	2.836(2)	3.994(2)	67.43	101.63	102.2
		−2.624(2)	−2.07(1)	−3.033(3)	−4.138(2)	−72.53	−111.31	−130.68
$[Cu_4I_4(pip)_4]$[c]	$\bar{4}$	2.691(1)	2.052(7)	2.630(2)	4.488(2)	58.20(5)	112.00(4)	104.2(2)
		−2.717(2)		−2.671(2)	−4.571(2)	−59.46(5)	−115.42(5)	−106.0(2)
$[\{Cu_4I_4(NEt_3)_3\}_\infty]$[d]	3	2.594(3)	2.08(3)	2.749(8)	4.313(5)	61.1(2)	102.4(2)	106.7(7)
		−2.940(10)	−2.14(3)	−3.086(7)	−4.426(5)	−69.6(2)	−115.5(2)	−113.7(8)
$[Cu_4Cl_4(PEt_3)_4]$[e]	$\bar{4}3m$	2.438(1)	2.176(2)	3.211(2)	3.657(2)	82.36(5)	97.15(4)	120.02(3)
$[Cu_4Br_4(PEt_3)_4]$[e]	$\bar{4}3m$	2.544(1)	2.199(4)	3.184(2)	3.932(1)	77.48(4)	101.25(3)	116.80(2)
$[Cu_4I_4(PEt_3)_4]$[f]	$\bar{4}3m$	2.684(1)	2.254(3)	2.927(2)	4.380(1)	66.10(4)	109.38(4)	109.56(8)
$[Cu_4I_4(AsEt_3)_4]$[f]	$\bar{4}3m$	2.677(2)	2.361(2)	2.783(2)	4.424(2)	62.63(5)	111.45(5)	107.41(6)
$[Ag_4I_4(NEt_3)_4]$[g]	$\bar{4}2m$	2.897(5)	2.37(3)	3.160(4)	4.677(5)	65.9(1)	110.4(1)	108.6(8)
		2.916(2)		3.224(5)	4.773(4)	67.6(1)	106.6(1)	110.4(4)
$[Ag_4Cl_4(PEt_3)_4]$[h]	$\bar{4}3m$	2.648	2.390(2)	3.329(2)	3.926(3)	80.39(6)	88.20(6)	112.97(5)
				3.647(2)		−90.21(8)	−99.61(6)	−134.86(8)
$[Ag_4Br_4(PEt_3)_4]$[h]	$\bar{4}3m$	2.739	2.402(5)	3.286(5)	4.201(3)	75.73(10)	93.0(2)	110.3(2)
				3.570(6)		−83.8(2)	−104.0(1)	−129.2(3)
$[Ag_4I_4(PEt_3)_4]$[i]	$\bar{4}2m$	2.918 4(9)	2.438(2)	3.198(1)	4.767 6(9)	66.44(2)	108.00(2)	109.13(6)
				3.229(1)	4.722 9(11)	67.15(2)	109.52(2)	110.33(3)
$[Cu_4Br_4(PBu^t_3)_4]$[j]	3	2.571(1)	2.228(4)	3.479(2)	3.827(1)	83.95(5)	94.70(5)	120.84(8)
		−2.604(1)		−3.491(2)	−3.838(1)	−84.85(5)	−95.74(5)	−122.43(8)
$[Cu_4Cl_4(PPh_3)_4]$[k]	2	2.363(2)	2.192(2)	3.118(1)	3.060(3)	79.71(6)	88.94(6)	112.73(7)
		−2.505(2)	−2.193(2)	−3.430(2)	−3.722(3)	−90.19(6)	−101.11(7)	−131.06(8)
$[Cu_4Br_4(PPh_3)_4]$[l]	2	2.491(2)	2.206(3)	3.087(2)	3.617(2)	74.96(5)	90.24(6)	111.73(8)
		−2.617(2)	2.209(3)	−3.541(2)	−4.004(2)	−87.85(5)	−105.55(6)	−127.27(9)
$[Cu_4I_4(PPh_3)_4]$[a]	1	2.653(3)	2.251(6)	2.874(5)	4.234(2)	67.78(9)	103.0(1)	106.5(1)
		−2.732(3)	−2.258(7)	−3.164(4)	−4.496(3)	−71.75(9)	−115.0(1)	−116.9(2)
$[Cu_4I_4(AsPh_3)_4]\cdot C_6H_6$[m]	1	2.667(2)	2.366(3)	2.781(3)	4.314(2)	61.99(6)	107.04(8)	101.22(8)
		−2.724(2)	−2.384(3)	−2.900(3)	−4.515(2)	−65.72(7)	−114.53(8)	−112.06(9)
$[Ag_4Cl_4(PPh_3)_4]$[n]	2	2.532(3)	2.376(3)	3.408(1)	3.649(5)	79.32(7)	87.23(8)	109.88(9)
		−2.760(3)	−2.388(3)	−3.797(1)	−4.031(3)	−92.67(8)	−101.20(8)	−138.85(9)
$[Ag_4Br_4(PPh_3)_4]$[o]	3	2.677(1)	2.415(5)	3.719(2)	3.964(2)	82.35(3)	89.19(3)	106.94(6)
		−2.962(1)	−2.429(2)	−3.930(1)	−4.200(1)	−92.39(5)	−100.29(4)	−142.36(6)
$[Ag_4I_4(PPh_3)_4]$[p]	1	2.836(2)	2.455(4)	3.115(2)	4.399(1)	64.53(4)	95.16(5)	104.07(11)
		−3.037(2)	−2.462(5)	−3.768(2)	−4.801(2)	−81.07(5)	−115.38(5)	−123.53(12)

[a] This work. [b] Ref. 16. [c] Ref. 11. [d] Ref. 14. [e] M. R. Churchill, B. G. De Boer, and S. J. Mendak, *Inorg. Chem.*, 1975, **14**, 2041. [f] M. R. Churchill and K. Kalra, *Inorg. Chem.*, 1974, **13**, 1899. [g] P. C. Healy, N. K. Mills, and A. H. White, *Aust. J. Chem.*, 1983, **36**, 1851. [h] M. R. Churchill, J. Donahue, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 2752; disordered metal atom. [i] M. R. Churchill and B. G. Boer, *Inorg. Chem.*, 1975, **14**, 2502. [j] R. G. Goel and A. L. Beauchamp, *Inorg. Chem.*, 1983, **22**, 395. [k] Ref. 5. [l] Ref. 8. [m] Ref. 22. [n] Ref. 2. [o] Ref. 3. [p] Ref. 4.

core distances and angles for (1) are given in Tables 5 and 6], along with complexes of the YEt_3 (Y = N, P, or As) base systems. In spite of the doubt cast over the usefulness of any attempted rationalization of cubane/step relative stabilities in terms of a simple steric model, the detailed analysis carried out on the basis of less complete structural data, in regard to trends and correlations amongst core parameters in the cubane system in terms of variations in metal, ligand, and halide,[2] remain valid.

The solid-state [31]P n.m.r. spectrum for this complex, together with that of a desolvated sample of the step isomer is reproduced in Figure 3. In both compounds, Cu–P quadrupolar interactions split the resonance signal for each of the crystallographically independent phosphorus nuclei into four.[23,24] The magnitude of the splitting, Δv_i, between the lines in each quartet is a function of both Cu–P scalar coupling and Cu–P dipolar and J-tensor interactions which are not averaged out by the magic-angle spinning techniques. These latter effects can give rise to a marked increase in Δv_i towards higher fields. The value of $\Delta v_i(max.) - \Delta v_i(min.)$, Δv_{ij}, can be correlated with the symmetry of the copper environment ($\Delta v_{ij} \approx 0$ for T_d symmetry).

For the cubane complex, the spectrum consists of two quartets in an intensity ratio of (A):(B) $\approx$ 3:1. Chemical shifts: (A) −1.2, −12.8, −25.8, −39.2, average $\langle \delta \rangle$ −19.8; (B) −7.9, −19.3, −32.1, −45.6, $\langle \delta \rangle$ −26.2 p.p.m. Splitting parameters: (A), $\Delta v_i = 1\,410$, 1 580, 1 680, $\Delta v_{ij} = 270$; (B), $\Delta v_i = 1\,390$, 1 560, 1 630, $\Delta v_{ij} = 240$ Hz.

The average values for the chemical shift suggest that in these complexes the PPh_3 phosphorus atoms are considerably more shielded in this cubane complex than in the free triphenylphosphine ligand [solid state $\delta(P)$ −9.9 p.p.m.]. The values of Δv_{ij} are also consistent with the phosphorus atoms being bound to a copper atom in a pseudo tetrahedral environment {cf. $[CuI(PPh_3)_2]$, approx. C_{2v} symmetry, $\Delta v_i = 920$, 1 230, 1 390, $\Delta v_{ij} = 470$ Hz; $[CuI(PPh_3)_3]$, approx. C_{3v} symmetry, $\Delta v_i = 900$, 930, 920, $\Delta v_{ij} = 30$ Hz}.[25] The structural results show that the chemical environment of each phosphorus atom with respect to its copper atom is very similar (Table 4) and, were this the only factor involved in determining chemical shift, only one quartet might have been expected, despite the presence of four crystallographically independent phosphorus nuclei in the unit cell. However, in the present case, significant variation in the
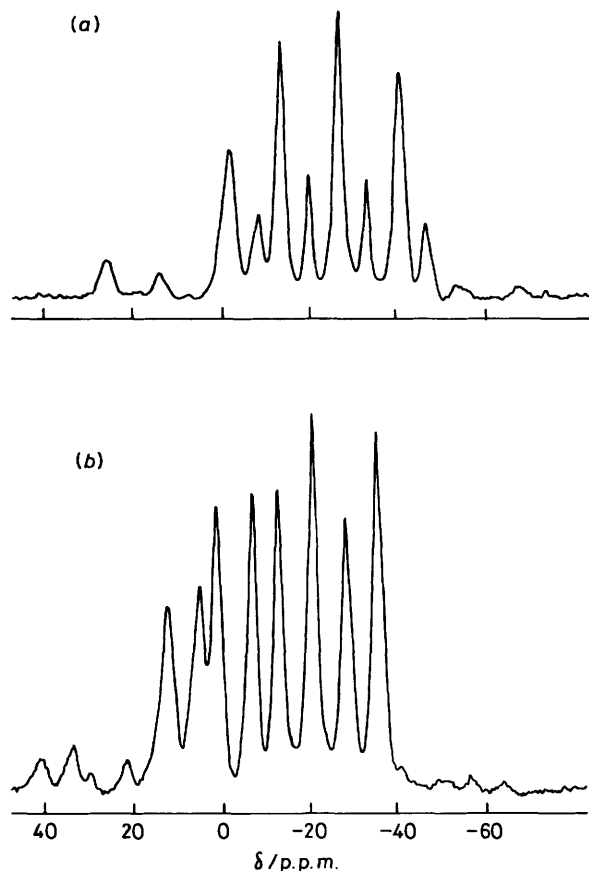
(a)

(b)

40   20   0   -20   -40   -60

δ / p.p. m.

Figure 3. Solid-state [31]P n.m.r. spectra of (a) cubane and (b) unsolvated step forms of $[Cu_4I_4(PPh_3)_4]$. The spinning side-bands observed on either side of the main signal indicate the existence of considerable ^{31}P chemical shift anisotropy. Peaks due to [65]Cu are not resolved

Table 5. Cu_4I_4 core distances (Å) in (1)

I(1)–Cu(2)	2.705(3)	I(3) ··· I(4)	4.480(3)
I(1)–Cu(3)	2.668(3)	I(4)–Cu(1)	2.664(3)
I(1)–Cu(4)	2.707(3)	I(4)–Cu(2)	2.708(3)
I(1) ··· I(2)	4.496(3)	I(4)–Cu(4)	2.692(3)
I(1) ··· I(3)	4.266(3)	Cu(1) ··· Cu(2)	2.930(4)
I(1) ··· I(4)	4.234(2)	Cu(1) ··· Cu(3)	2.898(4)
I(2)–Cu(1)	2.732(3)	Cu(1) ··· Cu(4)	2.874(5)
I(2)–Cu(2)	2.687(4)	Cu(1)–P(1)	2.258(7)
I(2)–Cu(3)	2.663(4)	Cu(2) ··· Cu(3)	2.839(4)
I(2) ··· I(3)	4.351(3)	Cu(2) ··· Cu(4)	3.164(4)
I(2) ··· I(4)	4.387(3)	Cu(2)–P(2)	2.251(6)
I(3)–Cu(1)	2.653(3)	Cu(3) ··· Cu(4)	3.109(4)
I(3)–Cu(3)	2.700(4)	Cu(3)–P(3)	2.252(7)
I(3)–Cu(4)	2.717(3)	Cu(4)–P(4)	2.255(8)

C–P–C angles and the relative orientations of the benzene rings (Table 7) for each ligand may well play an important role in determining chemical shifts. At this stage we are not in a position to assign confidently which phosphorus nucleus gives rise to each quartet. It is of interest to note that the relative intensities of the two quartets did not vary significantly in a series of experiments in which the spectra were recorded with differing ^{1}H–^{31}P contact times. This result is consistent with the very similar P–H distances found for each ligand [ligand 1: 2.77—2.90, average 2.83(5); ligand 2: 2.78—3.06, average 2.91(10); ligand 3: 2.82—2.97, average 2.91(6); ligand 4: 2.79—2.92, average 2.86(6) Å].

Like the cubane structure, the spectra of the desolvated step structure, $[Cu_4I_4(PPh_3)_4]$, reveal two quartets. However, the chemical shift values and relative intensities of these differ significantly from the cubane spectra, providing a very convenient method of identifying the two isomers. The chemical shift and splitting parameters for the compound are as follows: (A), δ 4.2, -7.6, -21.2, -36.0, $\langle\delta\rangle$ -15.2 p.p.m.; $\Delta v_i =$ 1 430, 1 650, 1 770, $\Delta v_{ij} = 340$ Hz. (B), δ 11.5, 0.5, -13.5, -28.7, $\langle\delta\rangle$ -7.6 p.p.m., $\Delta v_i = 1$ 320, 1 700, 1 860, $\Delta v_{ij} = 540$ Hz. These results are consistent with the single-crystal X-ray diffraction analysis of the chloroform-solvated step structure which reveals two independent phosphorus atoms bound to three- and four-co-ordinate copper atoms respectively, with significantly different Cu–P bond lengths: 2.228(5) and 2.242(4) Å. The variation in co-ordination number of the copper atom has only a small effect on the values of Δv_i. However, the larger value of Δv_{ij} observed for the second quartet may indicate that

this arises from the phosphorus atom bound to the three-co-ordinate copper atom. We are actively investigating the general validity of this assignment in a range of less complex three- and four-co-ordinate triphenylphosphine–copper(I) halide systems.

The single-crystal structure determinations establish the colourless crystalline complexes obtained by the recrystallization of copper(I) chloride and bromide from triethylamine, and of copper(I) chloride from 2-[bis(trimethylsilyl)methyl]pyridine to be the 1:1 adducts in all three cases. The molecular aggregates are tetramers with the Cu_4X_4 arrays comprising the familiar stellaoctangular pseudo-cubane disposition. This is the first time such an array has been found for the combination of copper(I) chloride with a nitrogen base, and is only the second report for a bromide derivative (see ref. 16). The array of (2) and (3) is of interest in regard to the observed isomorphism with the phosphine and arsine analogues, and also in view of the fact that the complex obtained by the recrystallization of the iodide from triethylamine is not the 1:1 adduct but the 1:0.75 adduct with the linked cube polymer structure. The (crystallographically imposed) symmetry of the $Cu_4X_4N_4$ unit in (2) and (3) is high, being 43m, and only one independent distance is found between any pair of atoms; these are given in Table 4 in which comparison is also made with the parameters of related systems. The geometry of the $[Cu_4I_4(pip)_4]$ species is included, piperidine (pip) being an aliphatic rather than aromatic substituted base, since the triethylamine adduct of copper(I) iodide is of anomalous stoicheiometry. Also included are data for $[Cu_4Br_4(2Me-py)_4]$. Of interest is the observation that the Cu–X distances are closely comparable with those observed in the counterpart complexes with triethylphosphine ligands; appreciable changes are observed, however, in the metal–metal distances which are shorter in the nitrogen base complexes, and the associated angular geometries. Finally, we note that all structurally studied $[Cu_4X_4(YEt_3)_4]$ (Y = N, P, or As) species are isomorphous and isostructural.

With pyridine ligands substituted in the 2- and 6-positions, a tendency toward disruption of the Cu_4X_4 core is evident, this being achieved with substitution in both positions in the 1:1 adduct of copper(I) iodide with 2,6-dimethylpyridine, a di-μ-iodo-bridged dimer,[17] while with the acridine derivative, a one-dimensional polymer is achieved.[14] Incipient disruption of the cube may be observed in the 2-methylpyridine 1:1 adducts of copper(I) iodide and bromide [Cu ··· Cu 2.674—2.729(7)[14] and 2.836(2)—3.033(2) Å[16] respectively]; the present 1:1 adduct of copper(I) chloride with a pyridine base strongly hindered in the 2-position complements this series, yielding one of the most distorted cubane arrays yet described. In $[CuCl_4(NEt_3)_4]$ bond lengths are Cu–Cl 2.441(4), Cu–N 2.054(5), Cu ··· Cu 3.069(1), and Cl ··· Cl 3.764(2) Å; those for $[Cu_4Cl_4(tmspy)_4]$ are Cu–Cl 2.225(2), 2.610(2), and 2.636(2), Cu ··· Cu 2.960(2) and 3.194(2),

Table 6. Cu_4I_4 core angles (°) in (1); each entry in the matrix is the angle subtended by the atoms at the head of the relevant row and column

	Cu(1)	I(2)	I(3)	I(4)	Cu(2)	Cu(3)	Cu(4)
I(3)	107.8(1)						
I(4)	108.8(1)	114.8(1)					
Cu(2)	56.5(1)	107.5(1)	57.7(1)				
Cu(3)	56.4(1)	58.0(1)	106.0(1)	58.3(1)			
Cu(4)	112.5(1)	58.7(1)	58.0(1)	66.1(1)	65.2(1)		
P(1)	106.5(2)	112.0(2)	106.5(2)	140.3(2)	146.9(2)	140.8(2)	

	Cu(2)	I(1)	I(2)	I(4)	Cu(1)	Cu(3)	Cu(4)
I(2)	113.0(1)						
I(4)	103.0(1)	108.8(1)					
Cu(1)	100.9(1)	58.0(1)	56.2(1)				
Cu(3)	57.5(1)	57.5(1)	106.5(1)	60.3(1)			
Cu(4)	54.2(1)	105.4(1)	53.9(1)	56.1(1)	62.1(1)		
P(2)	109.9(2)	109.1(2)	113.0(2)	149.1(2)	140.5(2)	145.5(2)	

	Cu(3)	I(1)	I(2)	I(3)	Cu(1)	Cu(2)	Cu(4)
I(2)	115.0(1)						
I(3)	105.2(1)	108.4(1)					
Cu(1)	102.6(1)	58.7(1)	56.4(1)				
Cu(2)	58.7(1)	58.4(1)	108.9(1)	61.4(1)			
Cu(4)	55.2(1)	107.5(1)	55.2(1)	57.0(1)	64.1(1)		
P(3)	113.1(2)	107.6(2)	107.0(2)	144.0(2)	144.1(2)	144.3(2)	

	Cu(4)	I(1)	I(3)	I(4)	Cu(1)	Cu(2)	Cu(3)
I(3)	103.7(1)						
I(4)	103.3(1)	111.8(1)					
Cu(1)	102.2(1)	56.6(1)	57.1(1)				
Cu(2)	54.2(1)	99.7(1)	54.4(1)	57.8(1)			
Cu(3)	54.1(1)	54.7(1)	99.7(1)	57.8(1)	53.8(1)		
P(4)	113.0(2)	116.9(2)	107.3(2)	144.3(2)	143.3(2)	152.4(2)	

Ranges (°): I–Cu–I, 103.0(1)—115.0(1); P–Cu–I, 106.5(1)—116.9(2); I–Cu–Cu, 54.1(1)—58.7(1) and 99.7(1)—112.5(1); Cu–Cu–Cu, 53.8(1)—66.1(1); P–Cu–Cu, 140.3(2)—152.4(2)

Table 7. Angles (°) between the normals to the rings A, B, and C and the normal to the base of the phosphorus pyramid in (1)

	Ligand 1	Ligand 2	Ligand 3	Ligand 4	PPh$_3$*
Ring A	128.7	67.3	51.9	106.5	68.0
Ring B	68.9	43.6	69.3	79.2	36.1
Ring C	37.4	34.6	34.9	21.5	65.3

* Parent ligand, see J. J. Daly, *J. Chem. Soc.*, 1964, 3799.

Table 8. Molecular core geometry of (4)

Distances (Å)

Cu–Cl	2.610(2)	Cu $\cdots$ Cu^{iii}	2.960(2)
Cu–Cl^i	2.636(2)	Cl $\cdots$ Cl^i	3.838(3)
Cu–Cl^{ii}	2.225(2)	Cl $\cdots$ Cl^{iii}	3.866(3)
Cu $\cdots$ Cu^i	3.194(2)	Cu–N(1)	1.986(5)

Angles (°)

Cl–Cu–Cl^i	94.07(7)	Cl^{ii}–Cu–N	138.8(2)
Cl–Cu–Cl^{ii}	104.82(8)	Cu–Cl–Cu^i	82.28(7)
Cl^i–Cu–Cl^{ii}	105.09(8)	Cu–Cl–Cu^{ii}	75.02(6)
Cl–Cu–N	102.5(2)	Cu^i–Cl–Cu^{iii}	74.51(6)
Cl^i–Cu–N	103.1(2)		

Transformations of the asymmetric unit: i $y - \frac{1}{4}$, $\frac{1}{4} - x$, $1\frac{1}{4} - z$; ii $\frac{1}{4} - y$, $\frac{1}{4} + x$, $1\frac{1}{4} - z$; iii $-x$, $\frac{1}{2} - y$, z

Cl $\cdots$ Cl 3.838(3) and 3.866(3) Å (Tables 4 and 8). The Cu–N distance is appreciably shortened in (4) being 1.986(5) Å. In contrast is the evenness of the Cl_4 interchlorine distances, indicating that the distortion is primarily achieved by rotation and distortion of the Cu_4 unit within the halogen framework; the extent of this distortion is readily appreciated from Figure 2, as is the asymmetry of attachment of the pyridine base at the copper atom, and also at the nitrogen atom. Cl–Cu–N angles range from 102.5(2) to 138.8(2)°, while Cu–N(1)–C(2,6) are 115.8(5), 124.9(4)° respectively. In spite of this evidence of considerable strain involved in the bonding of this ligand to the Cu_4Cl_4 core, it is noteworthy that the Cu–N distance is the *shortest* yet observed in such tetrameric systems (Table 4); in spite of this evidence of strong metal–ligand interaction, no further complexes of the type $[(CuClL)_n]$ ($n > 1$) appear to be formed since the present complex was obtained by recrystallization from a concentrated solution of excess base.

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